Deformation Behavior of Extruded Blown Film of High Density Polyethylene (STATES AND STRUCTURES-Polymer Condensed States)

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Deformation behavior of extruded blown film of polyetylene, which contains oriented lamellae normal to the extruded direction (MD), is investigated by scanning electron microscope and X-ray scattering techniques. Type of structural change in deformation process strongly depends on angle between stretching direction and MD. A structural model is proposed to explain the experimental results systematically.

Keywords : High density polyethylene / Extruded blown film/ Deformation / SEM/ X-ray diffraction

Deformation process of semi-crystalline polymers is strongly influenced by temperature and orientation of crystalline lamellae with respect to deformation direction. Aims of this study are to clarify mechanisms for unfolding of polymer chains, and to elucidate change from lamellar structure to fiber structure in deformation process. Extruded blown (EB) film of high density polyethylene (HD-PE) contains oriented crystalline lamellae, where polymer chains are parallel to extruded direction (MD:machine direction) and they are folding in ca.18nm thickness. In other words, the lamellae are originally oriented in direction normal to the extrusion direction (TD:transverse direction). There have been many investigations concerning deformation behavior of polyethylene [1,2]. In these studies, the stretching direction was perpendicular to original orientation of polymer chains. In this study, stretching of the EB film of HD-PE in various directions (involving parallel one to MD) is conducted, and the structural changes during the deformations are studied by X-ray scattering measurements and scanning electron microscopy (SEM).

HD-PE (Sholex 6009) was melted at 180°C and extruded from a circular orifice into air. Crystallization proceeded under elongation stress by drawing ratio of about 56 times. From the resultant films, specimens for mechanical and X-ray measurements were cut to obtain strips in various directions to MD. After the measurements, specimens were treated with fuming nitric acid for SEM observations (HITACHI S-310).

SEM observation shows that these films feature ordered stacking of untwisted lamellar crystals normal to MD (Fig.1). The thickness of a lamellar observed in SEM was about 100nm, while that from long period based on two-point diagram in SAXS pattern was about 18nm ((a) in Fig.1). These results suggest 5-6 sheets of folding of chain. Recently, we observed a lamella of about 18nm in AFM [3] in accord with the SAXS result. Stress-strain (S-S) curves are found to be much different per elongation direction. In the elongation along TD, the stress suddenly decreased when the film was elongated to the yield point, and thereafter the necking propagated steadily with a constant stress value. Optical observation revealed that necking boundary line was very sharp and perpendicular to elongation direction (parallel to MD) [4]. These deformation behavior are well explained by Kobayashi's silk hat model assuming that the polymer chains are pulled out of lamellae by unfolding [5]. In the elongation along MD, on the contrary, the film was apparently uniformly elongated without significant decrease of stress at the yield point. The necking boundary lines appeared at oblique angles about ±50° to MD due to the lamellar slipping, and gradual increase in number of necking line was observed during the drawing. In spite of these necking, shapes of the S-S curves were smooth, but the micronecking occurred one after another in many parts over the specimens.

Figure 1 shows a SEM image for EB film in the undeformed state. "A" in Fig. 1 shows the long connecting line of overlap-

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Scope of research

Attempts have been made to elucidate the molecular arrangement and the mechanism of structural formation/change in crystalline polymer solids, polymer gels and elastomers, polymer liquid crystals, and polymer composites, mainly by electron microscopy and/or X-ray diffraction/scattering. The major subjects are: synthesis and structural analysis of polymer composite materials, preparation and characterization of polymer gels and elastomeric materials, structural analysis of crystalline polymer solids by direct observation at molecular level resolution, and in situ *studies on structural formation/change in crystalline polymer solids.*

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ping parts of lamellae grown from different nucleus, and they pile alternatively. Probably, straight chains are assumed to be interpenetrating into center parts of lamellae (shish parts of Pennings' shish-kebab [6]) in EB film. Figure 2 indicates a SEM image for necked EB film drawn parallel to MD. It is found that oriented lamellae parallel to elongation direction appear by elongation instead of "A" in Fig.1. The parts corresponding to "A" in Fig. 1 and straight chains are first elongated and then the lamellae are bended, twisted, or rotated by the stress. By further stretching, tie molecules or link-fibrils [7] which link between lamellae are cut and the distance between lamellae is widen and lamellae orientation is changed to the stretching direction, and consequently the film is elongated by unfolding same as TD elongation [8].

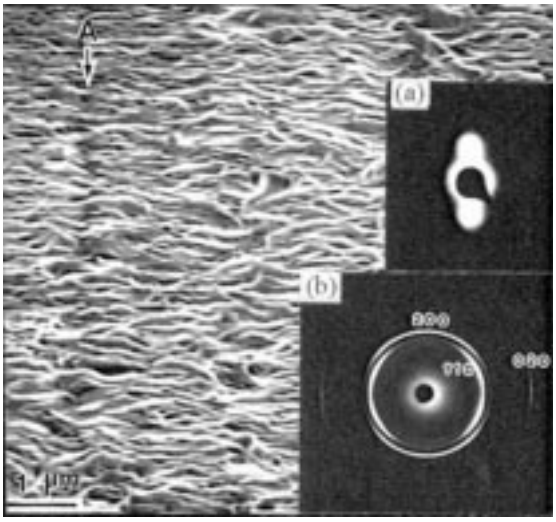

Figure 1. SEM of EB film etched with fuming HNO_3. (a) is SAXS pattern of two-point diagram showing long period of about 18nm. (b) shows WAXD pattern with X-ray beam normal to surface of film.

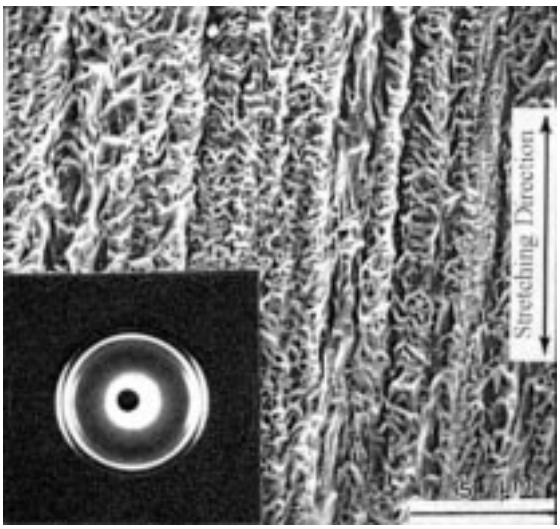

Figure 2. SEM of necked EB film drawn parallel to MD at room temp. Inset shows WAXD pattern whose most inner diffraction is 001 monoclinic one.

It was found by time-resolved X-ray diffraction patterns that the deformations induced phase transformation from orthorhombic to monoclinic form whose reflection appeared transiently inside orthorhombic 110 reflection during stretching at the temperatures below 50°C, as is shown in Fig. 2 [9]. This 001 monoclinic reflection (here b-axis is taken as fiber axis which is according to Seto et al. [10]) plane corresponds to orthorhombic 110 one, and the reflection appears in the stretching parallel to MD. The monoclinic reflection appeared from just before the onset of necking. However, in the stretching parallel to TD, monoclinic reflection did not appear. This is explained by assuming that the phase transformation occurs at a point of lamellae and no distortions such as bending, twisting and rotating occur in any other parts of lamellae. It should be noted that the b-axis is the growing direction of lamellae and parallel to TD. In the stretching to this direction, the transformation of lamellar structure to fiber structure appears to occur via successive unfolding starting from one part of lamellae due to stress concentration in the film. On the other hand, in the stretching parallel to MD, the transform appeared at many parts in specimen accompanied by various types of distortion. Based on these observations and correlations between structural changes and stress-strain relations, a structural model for elongation process is newly proposed, which is shown schematically in Fig.3. The model can explain the experimental results obtained here, thus elucidating the deformation mechanism of semi-crystalline polymer films in general. Further investigations on this model are in progress at our laboratory.

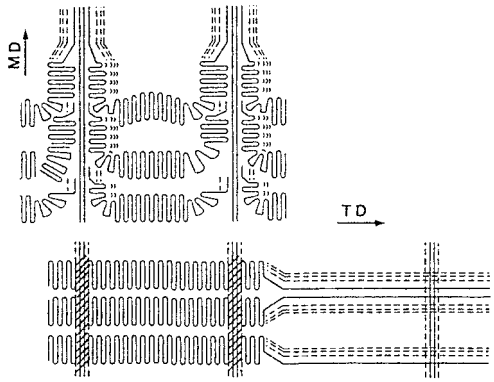

Figure 3. Structure model for chain-unfolding in stretching EB film.

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